

NO-A175 514

ELECTRON NUMBER DIAGRAM FOR STUDY OF CORROSION  
PROCESSES(U) CASE-WESTERN RESERVE UNIV CLEVELAND OH  
J C ANGUS ET AL. 26 SEP 86 ARO-21370.5-MS

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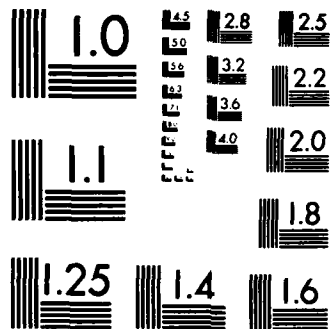
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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER <b>ARO 21370.5-A5</b>	2. GOVT ACCESSION NO. <b>N/A</b>	3. RECIPIENT'S CATALOG NUMBER <b>N/A</b>
4. TITLE (and Subtitle) <b>Electron Number Diagram for Study of Corrosion Processes</b>		5. TYPE OF REPORT & PERIOD COVERED <b>Final Report, 8/1/84-7/31/86</b>
AUTHOR(s) <b>John C. Angus and Michael J. Zappia</b>		6. PERFORMING ORG. REPORT NUMBER
PERFORMING ORGANIZATION NAME AND ADDRESS <b>Case Western Reserve University Cleveland, OH 44106</b>		7. CONTRACT OR GRANT NUMBER(s) <b>DAAG29-84-K-0094</b>
CONTROLLING OFFICE NAME AND ADDRESS <b>U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709</b>		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE <b>September 26, 1986</b>
		13. NUMBER OF PAGES <b>16</b>
		15. SECURITY CLASS. (of this report) <b>Unclassified</b>
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report)  <b>Approved for public release; distribution unlimited.</b>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)  <b>NA</b>		
18. SUPPLEMENTARY NOTES  <b>The view, opinions, and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.</b>		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)  <b>Corrosion, Phase Diagrams, Electron Number Diagrams, Thermodynamics,</b> <b>A</b>		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number)  <b>The theoretical and experimental foundations of electron number diagrams are being developed. These new diagrams provide a conceptual framework for interpreting and codifying the very complex chemical and phase equilibria which take place during practical corrosion processes. They also have utility in other areas such as electrodeposition, hydrometallurgy and geochemistry. Work has focused the single redox element systems Cu, Cr, Fe, S and U and the two redox element systems Ga/As and Cd/Te.</b>		

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## **1. PURPOSE OF THE RESEARCH**

The purpose of the research is to develop the theoretical and experimental basis of electron number diagrams, a new means for interpreting the complex redox equilibria important in corrosion processes.

## **2. RELEVANCE OF THE RESEARCH**

Electron number diagrams are a completely new type of phase diagram for use with aqueous redox systems. The diagrams codify information on phase stability in a form readily accessible to practicing corrosion engineers and scientists. Electron number diagrams provide an equilibrium framework within which corrosion systems can be described, analogous to the relationship of classical metallurgical phase diagrams to metal processing. In addition, the new diagrams will find use in such diverse fields as hydrometallurgy, sulfur removal processes, electrolytic processes and geochemistry.

## **3. SUMMARY OF MOST IMPORTANT RESULTS**

A listing of the most important results obtained during the research are listed below:

1. Development of the theoretical foundations and methods of application of electron number diagrams for single element redox systems (reference 2).
2. Development of activity/activity diagrams for interpretation of phase equilibria in complex aqueous systems containing two redox elements.
3. Development of efficient computer programs for generating electron number and potential-pH diagrams.

## **4. THEORETICAL AND COMPUTATIONAL WORK**

### **4.1 Principal Problems**

The principal problems that are being addressed include: 1) generation of a series of electron number diagrams for single redox element systems, 2) development of methods for treating systems containing two or more redox elements, 3) understanding of the relationship between the structure of the diagrams and the underlying detailed equilibrium solution chemistry, 4) development of diagrams for non-aqueous systems and 5) understanding the relationship between electron number diagrams and solid state theory.

During this reporting period we have made significant progress on items 1), 2) and 3) above. Much of this work has been reported in prior progress reports and in copies of publications forwarded to the sponsor (1,2,3,4). Here we primarily discuss recent work not previously reported.

## 4.2 Systems with One Redox Element

A series of electron number diagrams for single element redox systems have been constructed for the aqueous copper, iron, chromium, sulfur and uranium systems(2,4). Several examples of these diagrams are shown here.

In Figure 1 the electron number diagram for the aqueous copper system at pH = 6 and a chloride ion activity of 1.0 is shown. The evaporation trajectory of a solution initially containing  $10^{-5}$  molal total dissolved copper concentration is shown along the line PQS. The solution initially had an electron number of 1.5, i.e., equimolar amounts of  $\text{Cu}^+$  and  $\text{Cu}^{++}$  ions. (The electron number,  $\bar{z}$ , is defined in reference 2. For the present purposes it may be thought of as the number average valence.) If the evaporation is done in the absence of any oxidizing or reducing agents the average electron number remains constant at 1.5. When the concentration increases to approximately  $10^{-4}$  M (point Q), the solid phase  $\text{CuCl}_2 \cdot 3\text{Cu}(\text{OH})_2$  starts to precipitate. If evaporation is continued until point S is reached, the system is comprised of a solution at point R and the solid phase (point T). The relative amount of copper in the aqueous and solid phases is given by the inverse lever arm rule, i.e., the ratio ST/RS.

Also shown in Figure 1 is the trajectory taken when a solution containing  $10^{-2}$  M total dissolved copper is electroplated. This trajectory can be computed by a simple copper balance (2) and is shown along the curved line UVW.

The electron number diagram for the aqueous sulfur system at pH = 7 is shown in Figure 2. This system is distinguished by the fact that only one solid phase, elemental sulfur, can exist in equilibrium. The stability field for solid sulfur is given by the envelope GJK. Also shown in Figure 2 are lines of constant potential.

The use of electron number diagrams to describe mixing processes is illustrated in Figure 2. Consider the mixing of a solutions of  $\text{Na}_2\text{S}$  ( $\bar{z} = -2$ , point G) and a solution of  $\text{Na}_2\text{SO}_3$  ( $\bar{z} = +4$ , point I). If the solutions are mixed in a ratio of two moles of  $\text{Na}_2\text{S}$  to one mole of  $\text{Na}_2\text{SO}_3$ , the mixing point is at an average electron number of zero (point H). This clearly lies in the two phase envelope where solid sulfur precipitates. Since solid sulfur has an electron number of zero, and the overall electron number of the system is zero, it follows that the electron number of the solution must also be zero. The only point on the two phase envelope where the aqueous phase has a zero electron number is point J. This then must be the equilibrium point of the solution in equilibrium with the precipitated sulfur.

Figure 3 shows the electron number diagram for the aqueous chromium system at pH = 4. Several constant potential lines are also shown. The trajectory when a solution containing  $10^{-4}$  M total dissolved Cr is evaporated

at constant potential is shown along the line LMN. This would correspond to evaporation of a solution that was maintained in contact with an atmosphere containing approximately 0.05 ppm  $O_2$ .

Figure 4 shows an electron number diagram for the uranium system. This diagram is of interest because it shows the very complex phase behavior that can exist in a system such as uranium which can have many stable oxide phases.

#### 4.3 Systems with Two or More Redox Elements

One main outstanding problem remains the development of generalized methods for handling systems with two or more redox elements. We have obtained a partial solution for the problem, but still have much more to do on this aspect of the work. As example systems we have focused our attention on two particular two-element systems, Ga/As and Cd/Te. These systems are of unusual interest because of the possibility of electroplating the compounds GaAs and CdTe from aqueous solution. We are in the process of comparing the computed phase diagrams with published experimental work on electroplating these materials.

The solution to the two-redox element case is of more general interest to our program because it will permit us to treat common binary alloy systems, such as Fe/Cr and Fe/C.

#### 4.4 Computed Phase Diagrams for the Ga/As and Cd/Te Systems

Examples of computed diagrams for systems containing two redox elements (Ga/As and Cd/Te) are included as Figures 5 and 6. The diagram for Ga/As gives the stability field for compounds of Ga and As as a function of the total dissolved concentration of Ga and As. Constant potential lines (versus the standard hydrogen electrode) are also given. It is of considerable interest to note that there is a significant region where the compound GaAs is stable. However, at the pH of the figure (pH = 3), this occurs at potentials where hydrogen would be co-evolved if electrodeposition of GaAs were to be attempted.

The diagram for the Cd/Te system (Figure 6) shows only the stability field for the compound CdTe.

#### 4.5 Thermodynamic Analysis for Two Redox Element Systems

In this section we describe in some detail the thermodynamic analysis and computations for a two element system (Ga/As).

For an aqueous system containing two redox elements (at constant temperature and pressure), the phase rule becomes (3)

$$F = 5 - P \quad (1)$$

where F is the number of degrees of freedom and P is the number of phases. Fixing pH gives

$$F = 4 - P \quad (2)$$

Since the minimum number of phases is one, equation (2) shows that three dimensions are required to represent the equilibrium of a two redox element system at fixed  $T$ ,  $P$  and  $pH$ . The equilibrium can be represented in the three dimensional space  $\{a_M, a_N \text{ and } E\}$ , where  $a_M$  and  $a_N$  are the activities of elements  $M$  and  $N$ . The equilibrium of a single solid phase with the aqueous phase appears as a surface in this representation. These two phase surfaces intersect along three phase lines where two solid phases exist in equilibrium with the aqueous phase. These lines can come together at four phase invariant points, where three solids and the aqueous phase are present. The equilibrium figure divides the three dimensional space into a volume containing the undersaturated aqueous phase and an inaccessible volume, where solubility limits preclude equilibrium.

Equilibrium diagrams can be constructed for binary cases involving cross species (species that contain both redox elements). The aqueous Ga-As system will be considered as an example. This system contains one solid cross species, GaAs, and no dissolved cross species. The diagram will be constructed, assuming pure solid phases, at a fixed  $pH$  and a fixed activity of any complexing species  $X$ , e.g., reactive counter ions such as  $Cl^-$  or reactive gases such as  $NH_3$ . First, the equilibria for the Ga and As systems will be solved independently. Stability tests will then be used to determine where, if anywhere, the GaAs phase is stable.

For fixed  $pH$  and  $a_X$ , the three dimensional equilibrium figure for the aqueous Ga-As system can be projected onto a field of  $-\log_{10}[Ga]_{aq}$  vs.  $-\log_{10}[As]_{aq}$ . Figure 5 is such a diagram for the aqueous Ga-As system at a  $pH$  of 3 when no complexing species are considered. Two phase equilibrium surfaces project onto this type of diagram as areas. Four phase invariant points, where three solids coexist with the aqueous phase, are also possible on this type of diagram. For example, at point A on Figure 1, GaAs,  $Ga_2O_3$  and As are in equilibrium with the aqueous phase.

For a given  $E$ , the stable solid phase in the independent aqueous gallium system can be determined by minimizing  $(\mu_{Ga} - \mu_{Ga}^{\circ})$ , the chemical potential of elemental gallium in the system. The total dissolved gallium concentration,  $[Ga]_{aq}$ , in equilibrium with the stable solid phase can then be calculated. On a  $-\log_{10}[Ga]_{aq}$  vs.  $-\log_{10}[As]_{aq}$  diagram, the line along which the stable gallium solid is in equilibrium with the calculated  $[Ga]_{aq}$  would be horizontal—it is independent of  $[As]_{aq}$ . Note that this is also a constant potential line. At the same  $pH$  and  $E$  for the aqueous arsenic system,  $(\mu_{As} - \mu_{As}^{\circ})_{min}$ , the stable solid arsenic phase and  $[As]_{aq}$  can be determined. Along a vertical constant potential line on the a  $-\log_{10}[Ga]_{aq}$  vs.  $-\log_{10}[As]_{aq}$  diagram, the stable arsenic solid is in equilibrium with the calculated  $[As]_{aq}$ . The vertical constant potential line, along which an



arsenic solid is stable, and the horizontal line at the same potential, along which gallium solid is stable, intersect at a point at which the stable gallium solid, the stable arsenic solid and the aqueous phase are in equilibrium.

The stability of the cross solid GaAs depends on both  $\mu_{As}$  and  $\mu_{Ga}$  ( $\mu_{As}^{\circ} = \mu_{Ga}^{\circ} = 0$ ). Because we have assumed pure solid phases and  $p \approx 1$  atm.,

$$\mu_{GaAs} = \mu_{GaAs}^{\circ} \quad (3)$$

Thus, the condition for the equilibrium existence of GaAs in this system is

$$\mu_{GaAs}^{\circ} = \mu_{Ga} + \mu_{As} \quad (4)$$

The relationship between the total dissolved gallium activity and  $\mu_{Ga}$  is given by

$$\sum_i \left[ \gamma_i [Ga_i] \right]^{v_i} = \sum_i \exp \left[ \frac{\mu_{Ga} - \mu_{Ga}^{\circ}}{RT} + 2.30259 h_i(pH) + \frac{z_i F}{RT} (E - E_i^{\circ}) - x_i \ln a_X \right] \quad (5)$$

where the index  $i$  runs over the dissolved species containing gallium. Assuming all  $\gamma_i = 1$  and considering a case where all  $v_i = 1$ , this equation reduces to

$$[Ga]_{aq} = C_1 \cdot \exp \left[ \frac{\mu_{Ga} - \mu_{Ga}^{\circ}}{RT} \right] \quad (6)$$

where

$$C_1 = \sum_i \exp \left[ 2.30259 h_i(pH) + \frac{z_i F}{RT} (E - E_i^{\circ}) - x_i \ln a_X \right] \quad (7)$$

Notice that at fixed pH,  $E$  and activity of  $X$ ,  $C_1$  is a constant.

An analogous equation relating  $\mu_{As}$  and  $[As]_T$  can be obtained:

$$[As]_{aq} = C_2 \cdot \exp \left[ \frac{\mu_{As} - \mu_{As}^{\circ}}{RT} \right] \quad (8)$$

where

$$C_2 = \sum_j \exp \left[ 2.30259 h_j(\text{pH}) + \frac{z_j F}{RT} (E - E_j^0) - x_j \ln a_X \right] \quad (9)$$

and the index  $j$  runs over the dissolved arsenic species. These equations assume that all  $\gamma_j = 1$  and consider a case where all  $\nu_j = 1$ .

Substitution of Equations 6 and 8 into the equilibrium criterion for the existence of GaAs, as given in Equation 4, results in:

$$\frac{\mu_{\text{GaAs}}^0}{RT} = \ln \left[ \frac{[\text{Ga}]_{\text{aq}}}{C_1} \right] + \ln \left[ \frac{[\text{As}]_{\text{aq}}}{C_2} \right] \quad (10)$$

Equation 10 can be rewritten in the following form:

$$-\log_{10}[\text{Ga}]_{\text{aq}} = \log_{10}[\text{As}]_{\text{aq}} + \left[ \frac{-\mu_{\text{GaAs}}^0}{RT(\ln 10)} - \log_{10}(C_1 \cdot C_2) \right] \quad (11)$$

Note that the quantity in the large square brackets is a constant at fixed pH,  $E$  and  $a_X$ . Therefore, a constant potential line in a region of the diagram where GaAs is stable will be a straight line with a slope of  $-1$ , as shown by the above equation.

The current method for computing these diagrams uses Equations 4 through 10 to calculate points on the various possible three phase lines. Stability tests are then performed to determine which points should appear on the diagram. Equations 6, 8, 10 and 11 are all specific to the case where, for each dissolved species  $i$ ,  $\nu_i = 1$ . The aqueous cadmium-tellurium system contains

the ditelluride ion ( $\text{Te}_2^{2-}$ ); thus, these simplified equations do not apply.

Figure 6 is a projection of the region of stability of CdTe onto a field of  $-\log_{10}[\text{Te}]$  vs.  $-\log_{10}[\text{Cd}]$  for the aqueous Cd-Te system at pH = 7. Notice that the slopes of the constant potential lines in the stability region of CdTe are not constant.

A more efficient algorithm, which will be necessary to consider more complicated binary systems, is being developed. The basic idea of this method is to solve the equilibrium equations directly for the chemical potentials of the electrons and the two active elements in order to obtain explicit equations for the four phase invariant points. From these points, the three phase lines can be drawn efficiently.

## 5. EXPERIMENTAL WORK

Work on developing an experimental program to determine electron number diagrams in the laboratory was continued throughout the reporting period. These results will be used to confirm the computed electron number diagrams. This work will initially be directed at the two single-element systems, copper and sulfur. There is a good thermochemical data base for each of these systems and very interesting features occur at easily accessible experimental conditions in each system. Phase boundaries will be determined by monitoring the potential of the system along dilution trajectories, by electrochemical titration and, in the case of sulfur, by gravimetric analysis.

The experimental cell has been designed and the basic equipment necessary to perform the experiments has been received. The glove box system within which the sulfur experiments will be performed is operational. The experimental cells for the measurements on the copper system are still being set up. Some experiments on the sulfur system have been made, but the results are too preliminary to report here. No results on the copper system are available.

## 6. COMPUTER ALGORITHMS

The programs developed for computing potential-pH and electron number diagrams have been of interest to other research groups. Copies of the programs we use to compute potential-pH and electron number diagrams have been sent to a number of workers in this country and abroad. For example, workers in Britain are using the programs to study the phase chemistry of the aqueous vanadium/sulfur system.

The algorithms are all based on the "method of virtual species," which permits a sequential, rather than simultaneous, solution of the large number of equilibrium equations required to describe these systems. This method is described in detail in two publications by our research group (1,3).

## 7. SCIENTIFIC PERSONNEL ASSOCIATED WITH THE PROJECT

### 7.1 Personnel

Professor John C. Angus served as Principal Investigator and directed all phases of the research. Mr. Michael Zappia, a Ph.D. candidate in Chemical Engineering, was supported under the contract. Ms. Bei Lu worked in the same research area but was supported by other research funds (Department of Energy). Ms. Lu completed her M.S. degree and has left the project. Recently, Mr. Emil Schlabach, an M.S. candidate in Chemical Engineering joined the project. He also is supported by the Department of Energy.

### 7.2 Degrees Completed

Mr. Michael Zappia and Ms. Bei Lu completed M.S. degrees in Chemical Engineering while working on the project.

## 8. PUBLISHED PAPERS

The following papers were published during the course of the work supported under the present contract.

1. John C. Angus and Charles T. Angus, "Computation of Pourbaix Diagrams Using Virtual Species," J. Electrochem. Soc. 132(5), 1014-19, 1985.
2. John C. Angus and Michael J. Zappia, "Electron Number Diagrams: A New Phase Diagram for Complex Redox Systems," accepted for publication, J. Electrochem. Soc., 1986.
3. John C. Angus, Bei Lu and Michael J. Zappia, "Potential-pH Diagrams for Complex Systems," accepted for publication, J. Appl. Electrochem., 1986.
4. John C. Angus, Michael J. Zappia and Bei Lu, "Computed Phase Diagrams for Complex Aqueous/Solid Redox Systems: Applications to Corrosion Processes," Tri Services Conference on Corrosion, Orlando, FL, December 5, 1985.

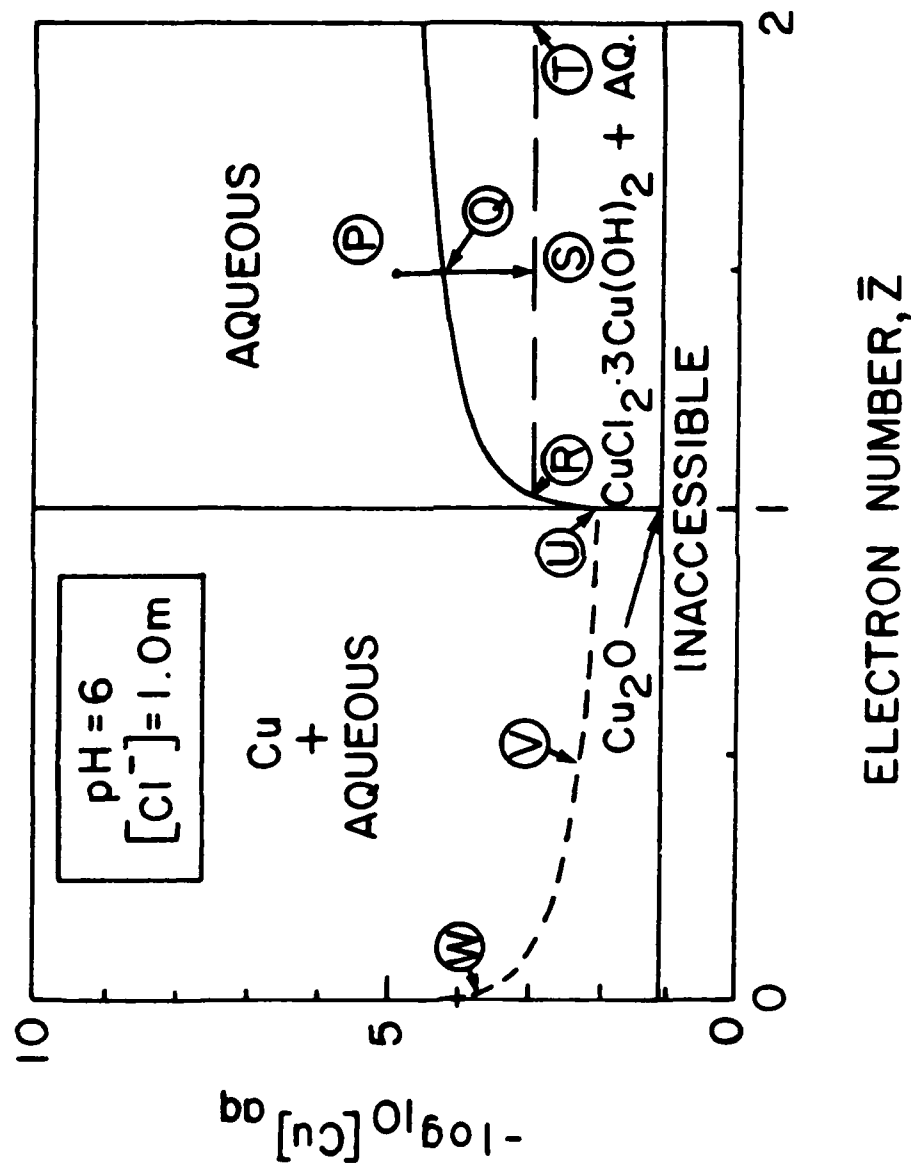


Figure 1. Electron Number Diagram for the Aqueous Copper System at  $\text{pH} = 6$  and chloride ion activity of 1.0. Evaporation trajectory PQS and electrolysis trajectory UVW are shown.

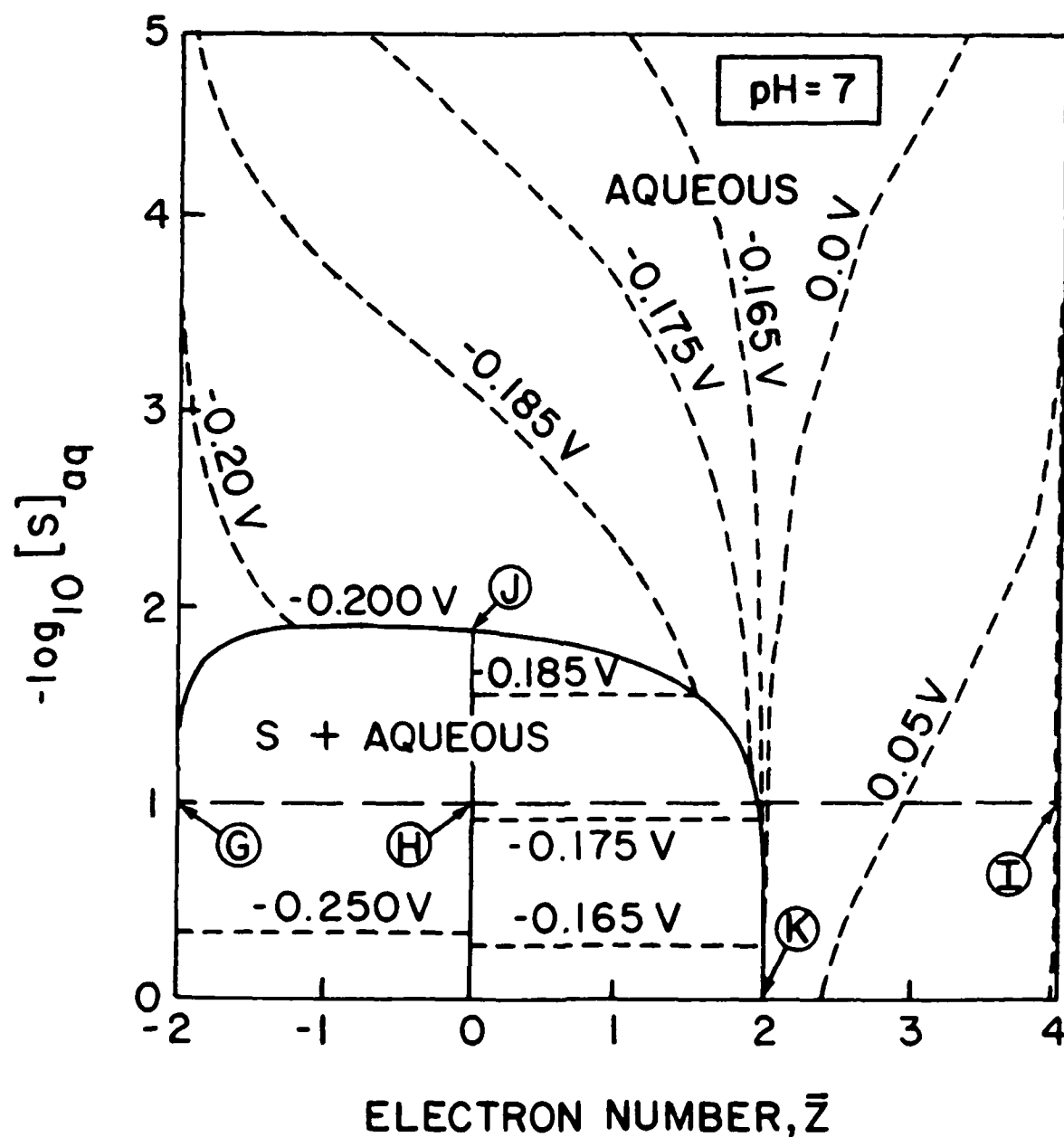


Figure 2. Electron Number Diagram for the Aqueous Sulfur System at  $pH = 7$ . The mixing of a 2/1 molar ratio of  $Na_2S$  ( $\bar{z} = -2$ , point G) and  $Na_2SO_3$  ( $\bar{z} = +4$ , point I) to form solid sulfur plus a solution at point J is illustrated.

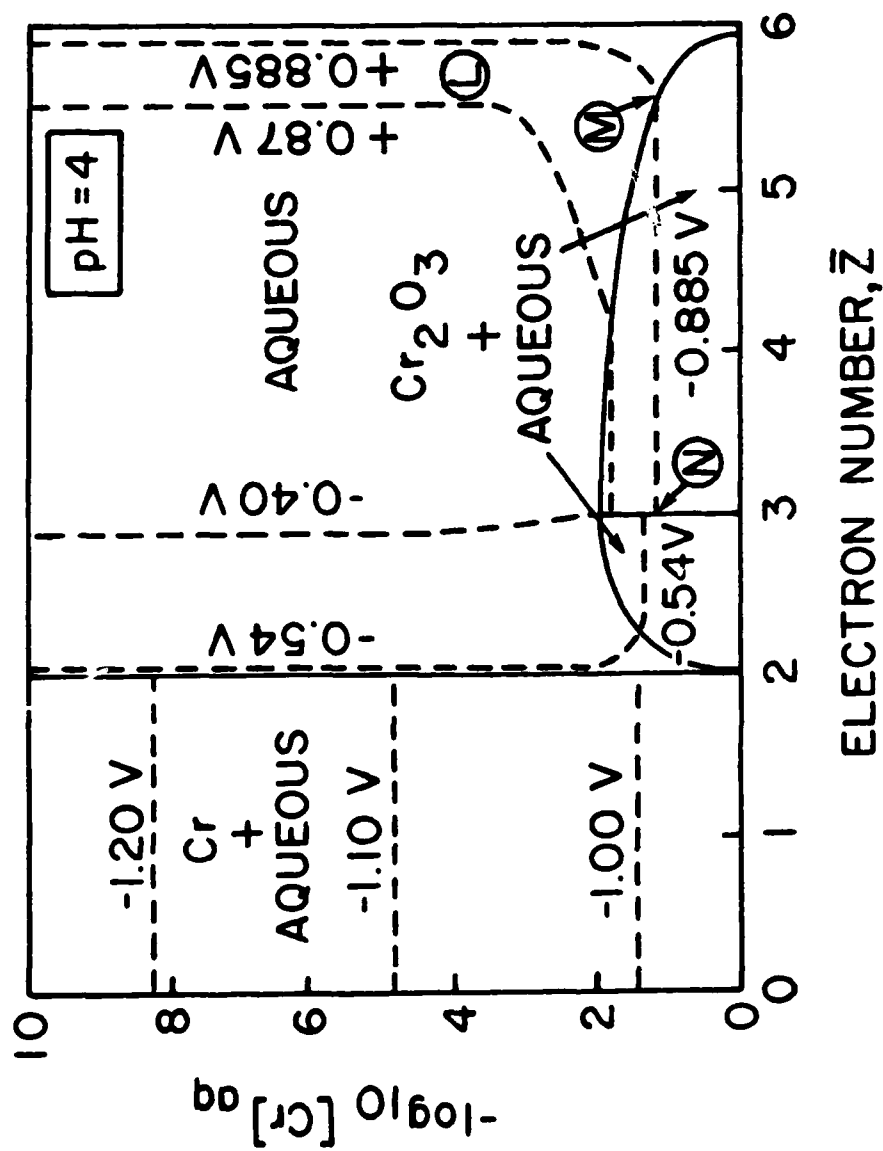


Figure 3. Electron Number Diagram for the Aqueous Chromium System at  $\text{pH} = 4$ . The evaporation trajectory at constant potential is shown along the curve LMN.

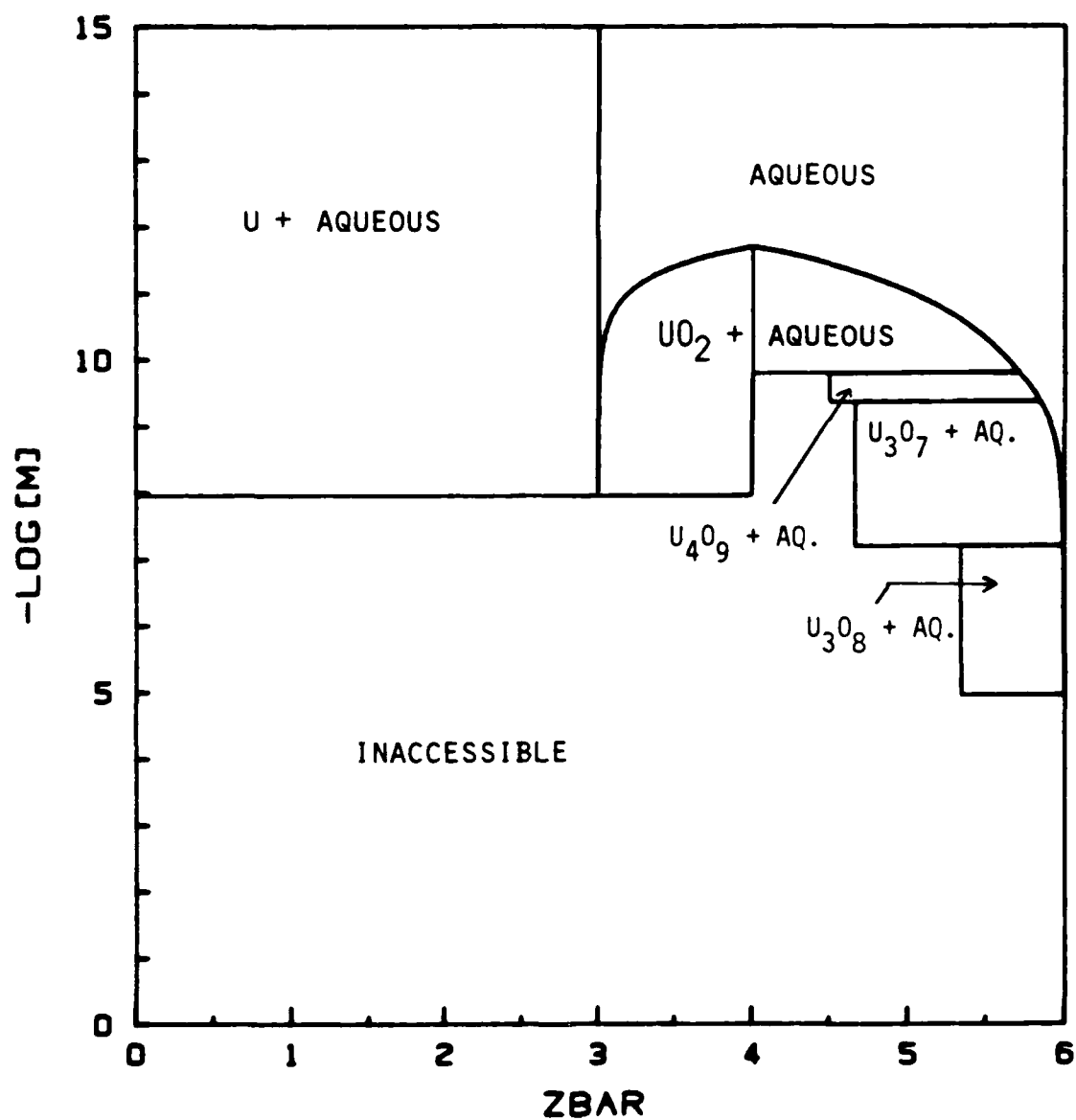


Figure 4. Electron Number Diagram for the Aqueous Uranium System. Note the complex phase behavior caused by the several stable oxide phases.



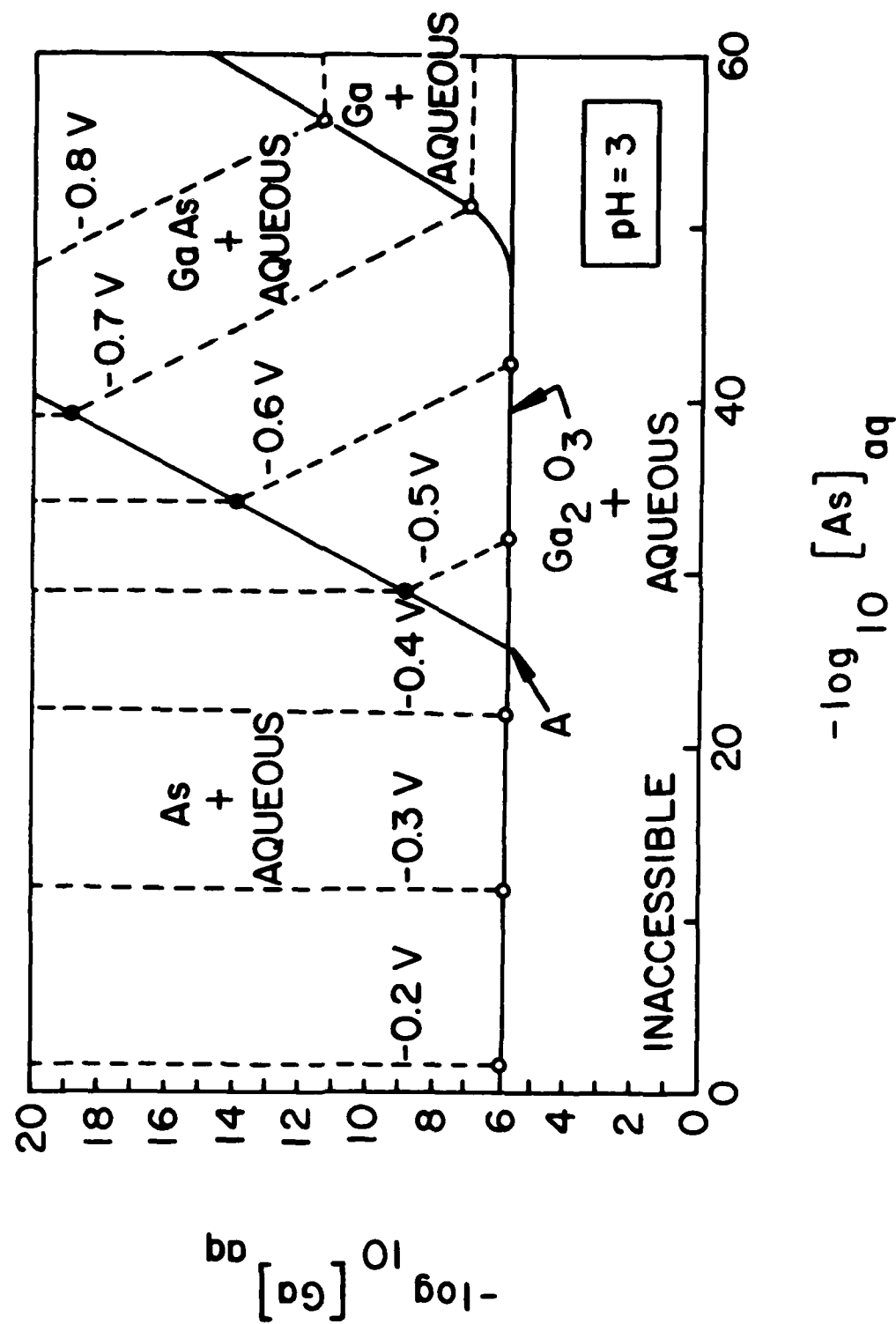


Figure 5. Activity/activity Diagram for the Aqueous Gallium/Arsenic System at pH = 3.

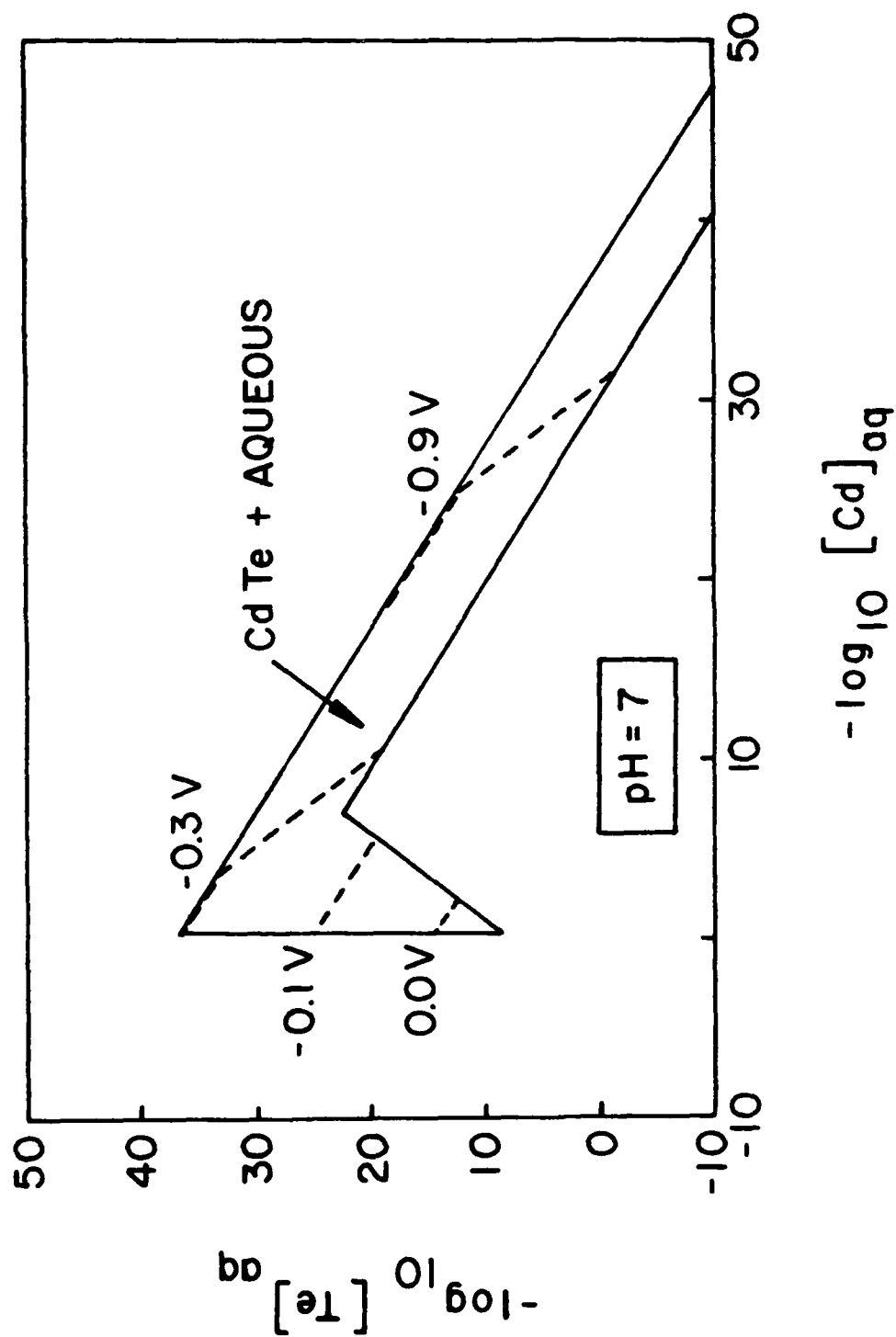


Figure 6. Activity/activity Diagram for the Aqueous Cadmium/Tellurium System at  $\text{pH} = 7$ .

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